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Iron metallurgy slags as a potential source of critical elements - Nb, Ta and REE

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Abstract. The recovery of valuable metals from metallurgical slag disposals is a promising option to protect natural resources, limited due to technology development and increased consumption. The Ad-hoc Working Group on Defining Critical Raw Materials within the Raw Materials Supply Group has proposed a list of critical elements which have the greatest economic importance and meet the requirements of sustainable development in Europe. The goal of this study was to examine steelmaking- and blast-furnace slags from metallurgical processes to determine concentrations of elements of the greatest criticality for Poland, e.g. Nb, Ta and REE, and to discuss the viability of their recovery. Slag analyses indicate enrichment of REE relative to UCC, NASC and average chondrite compositions in blast-furnace slags and Nb and Ta in steelmaking slags. To make recovery of these critical elements reasonable and profitable, it is recommended that they be recovered together with other useful raw materials.

Key-words: metallurgical slags, chemical composition, critical elements, Nb, Ta, REE

1. Introduction

The world economy is dependent on a constant supply of raw materials. Due to the technology development, the consumption of most metals is increasing and is expected to rise further. As natural resources of metals are limited, sustainable development is crucially dependent on securing new ore resources. Therefore, the Ad-hoc Working Group on Defining Critical Raw Materials within the Raw Materials Supply Group of the EU prepared a report on Critical Raw Materials for the EU (2010). Economic importance, and

the overall supply risk of selected raw materials as reflected in, e.g. their substitutability, recycling rates, and numbers of producing countries with poor governance, were the main criteria for choosing materials of most critical importance. The report, considered 41 non-energy and non-agricultural materials: tantalum, antimony, beryllium, cobalt, gallium, germanium, indium, magnesium, tungsten, niobium, Platinum Group Metals (PGMs): palladium, platinum, rhodium, ruthenium, iridium, and osmium, Rare Earths Elements (REE): scandium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, erbium, yttrium, holmium, erbium, thulium, ytterbium, and lutetium, fluorspar and natural graphite. A group of 14 critical raw materials was identified (Antimony, Beryllium, Cobalt, Fluorspar, Gallium, Germanium, Graphite, Indium, Magnesium, Niobium, PGMs, REEs, Tantalum, and Tungsten)

In 2013, 54 additional non-energy and non-agricultural materials were evaluated. The new list of 20 critical raw materials/metals includes almost all of those listed in 2010. Only tantalum, due to a lower supply risk, was deleted from the earlier list while six materials were added: borates, chromium, magnesite, coking coal, phosphate rock, and silicon metal (Report on Critical Raw Materials for the EU, 2014).

Currently, 90% of critical raw materials/elements is supplied by only 20 countries (Report on Critical Raw Materials for the EU, 2014). Of these, China, Russia, Turkey and the USA are among the most important suppliers to the European Union.

According to Smakowski (2011), the list is one of deficit raw materials with only three, namely niobium (Nb), tantalum (Ta) and REE, deserving to be called critical. These are difficult to substitute with other elements without either increasing costs significantly or decreasing product quality and performance (Silberglitt et al. 2013).

As Nb and Ta are metals of specialized use in technical fields, they are treated as strategic materials. The possibility for their recovery in the EU are scrapped products containing small recoverable amounts amounting to < 10% of demand (Smakowski 2011).

In Poland, phosphogypsum wastes are commonly considered a potential source of REE (e.g. Jarosiński 2016; Kulczycka et al. 2016). Kulczycka et al. (2016) have reported lanthanide contents (as Ln_2O_3) between 0.3-0.7% in phosphogypsum concentrate in which LREE dominates significantly over HREE. Jarosiński (2016) estimated that phosphogypsum waste from the “Wizów” Chemical Plant total containing 8280 t of REE in total included 200 t of Y and 33 t of Eu.

REE are used in the glass- and polishing industry (Ce), magnets (Sm, Nd), phosphors (Eu), catalysts (La), metallurgy (Ce) and in nuclear- and defense technologies (Meyer, Bras 2011; Smakowski, 2011; Gutiérrez-Gutiérrez et al. 2015). Up to 2011, recycling rates for REE were below 1% (Binnemans et al. 2013a,b; Graedel et al. 2011) but significant future increases in supply from secondary sources are to be expected (Schulze, Buchert 2016).

European countries are not self-sufficient to meet demands for consumption and technology development (Massari, Ruberti 2013). Shortages of critical materials require the optimization of recovery and recycling from residues, dumps, end-of-life consumer goods and landfilled waste streams to compensate for the deficiency (Binnemans et al. 2013a; Morf et al. 2013).

Raw-material processing and metallurgical treatments leads to the generation of substantial quantities of wastes that may contain valuable amounts of elements of interest. The presence of REE and other metals deemed critical have been described in sewage

sludge (Kawasaki et al. 1998), municipal solid waste (Morf et al. 2013), incineration products of other wastes (Zhang et al. 2001), metallurgical slags (Binnemans et al. 2013b), in the so-called “red mud” bauxite residue generated by the alumina refining industries (Liu, Naidu 2014), in electrical and electronic waste (e.g. Mueller et al. 2015; Sommer et al. 2015) and in slags (Zimmermann, Gößling-Reisemann 2013).

It is important to study the chemical composition of all these materials to prevent dissipative loss of metals from the end-of-life phase of metal-containing products. Slags, for instance, landfilled on waste heaps commonly come to be re-used in many ways, inhibiting the recovery of potentially valuable elements due to long residence times. With the present emphasis on recycling, more efficient recovery methods will likely be developed in the future.

The work presented here is an examination of iron metallurgical slags, both from steelmaking- and blast-furnace-processes. Contents of the critical elements listed by Smakowski (2011), and the feasibility and profitability of their recovery, are the focus. The annual production of iron-metallurgy slags in Poland, though lower than in the past, amounted to 2.6 Mg in 2014 (Statistical Yearbook of the Republic of Poland, 2014). However, the volume of landfilled slags remains large (3.7 Mg).

2. Materials and methods

2.1. Slag samples and their preparation

Steelmaking (S1, S2) and blast-furnace (B1, B2) slags differing in storage times (Table 1) were collected from two landfills located in Lesser Poland. 15 kg of each sample were crushed to ~ 0.4 cm in the Institute of Geological Sciences, Jagiellonian University, and then to ≤ 0.2 mm and averaged in the Laboratory of Separation and Mineral Enrichment, Institute of Geological Sciences, University of Wrocław. For chemical analysis, samples (20 g) of the averaged material were ground in an agate mill to the ≤ 0.02 mm fraction.

TABLE 1

Duration of landfilling of slags

Sample name	Time of landfilling (in years)
S1	5
S2	1
B1	5
B2	25

S1, S2 – steelmaking slag; B1, B2 – blast-furnace slag

To investigate the diversity of the chemical compositions of slags more in detail, the resulting data were compared with those of Małoszowski (2009), Jonczy and Lata (2013)

and Jonczy (2014). Małoszowski (2009) studied blast-furnace slags (W) collected from the area of the former ironworks in Kuźnice (Zakopane) which had operated in the eighteenth and nineteenth centuries. Jonczy (2014) presented chemical compositions of steelmaking slags (Martin process) produced between 1987-1995 by Huta Łabędy (JM), and of electric-arc furnace (EAF) and ladle-furnace (LF) slags from the current production of Ferrostal Łabędy Sp. z o.o. Jonczy and Lata (2013) presented chemical analyzes for both steelmaking- and blast-furnace slags collected from a dump in Dąbrowa Górnicza in Upper Silesia (JL).

2.2. Chemical analysis

The chemical analyses of the critical elements discussed in this paper were performed in the ACME Analytical Laboratories (Vancouver, Canada). Inductively coupled plasma mass spectrometry (ICP-MS) analyses were performed using Elan 9000, 6000 or Nexion 300 ICP machines to measure trace-element concentrations. Prior to analyses, 0.5 g of powdered sample was digested for 1 hour in a heating block or hot water bath using a modified Aqua Regia solution of equal parts of concentrated HCl, HNO₃ and deionized H₂O. Each sample was made up to volume with dilute HCl. Only the slags from Huta Łabędy and Ferrostal Łabędy Sp. z o. o. were analyzed by Activation Laboratories Ltd. (ACTLabs) in Canada.

Main mineral compositions of the slags S1, S2, B1 and B2 were determined by XRD using a Philips X'Pert (APD type) diffractometer with a PW 3020 vertical goniometer equipped with a curved graphite crystal monochromator (CuK α radiation, analytical range 2-64°2 θ , step 0.02°, duration 1 sec/step). Phase compositions were identified using Philips X'Pert software (associated with the ICDD database). The same diffractometer was used to determine main mineral compositions of the slag samples described in Małoszowski (2009) whereas a diffractometer with a HZG-4 goniometer equipped with a high voltage generator IRIS-3 and CuK α radiation was used to analyze the JM, JL, EAF and LF samples. Analytical details are in Jonczy (2014) and Jonczy and Lata (2013).

3. Results

3.1. Macroscopic characteristics of the slags

The steelmaking slag samples S1 and S2 are massive, dense, dark-brownish to greyish-brown in color and resemble basalt. S2 is the denser and more massive of the two. The samples are characterized by fragments of medium-size vesicles. On fresh fractures, it is possible to recognize elongated crystals of larnite and iron oxides.

The blast furnace slags B1 and B2 are vesicular and light grey in color. They are low density slags due to an abundance of pores of variable size, from 0.5 cm up to several cm in diameter. Macroscopically, it is difficult to recognize any slag components though secondary gypsum does occur in pores.

The blast-furnace slags collected by Małoszowski (2009) were divided into 5 groups distinguished by characteristics such as color, porosity and relative glass content. Group W1 was pale green with low porosity, W2 was black, porous and contained glass, W3 was dark green with medium porosity, W4 was brownish, glassy and very porous and W5 was

black, glassy but with low porosity. Jonczy (2014) described the slags from the dump in Huta Łabędy (JM) as characterized by light grey to grey color, fine-grained to middle-grained with a vesicular or compact texture with pores filled with secondary calcite. The EAF slags were black, with microcrystalline structure, porous and brittle, whereas the LF slags were light grey to greenish, with a dense microcrystalline structure. The macroscopic characteristics of the samples from the dump in Dąbrowa Górnicza (JL) are unknown.

3.2. Chemical characteristics of the slags

The concentrations of Nb, Ta and REE in six samples of steelmaking slag, nine blast-furnace samples, one sample of electric-arc furnace slag and one ladle-furnace slag from different localities in Poland are listed in Table 2.

The highest concentration of Nb was measured in the EAF slag sample (140 mg kg^{-1}) though high concentrations were also measured in the steelmaking slags, namely, 30.4 mg kg^{-1} in the S1 and 24.1 mg kg^{-1} in S2. In blast-furnace slags, Nb concentrations vary widely between samples but never exceed 15 mg kg^{-1} . Ta concentrations are highest in steelmaking slags, i.e. 12.4 mg kg^{-1} in JL1 and 6.8 mg kg^{-1} in JL2. In contrast, in S1 and S2, the Ta concentration does not exceed 1 mg kg^{-1} . In the blast furnace slags, the Ta concentration was $< 1 \text{ mg kg}^{-1}$ except in JL3 where it reached 2.5 mg kg^{-1} . Sc concentrations are very low in the steelmaking slags, whereas, in the blast-furnace slags, values up to 17 mg kg^{-1} were measured. Similarly, concentrations of Y are low in steelmaking slags whereas they exceed 30 mg kg^{-1} in blast-furnace slags.

REE concentrations are very low in steelmaking slag; they do not exceed a few mg kg^{-1} . W3 shows the highest concentrations for LREE among blast-furnace slags, namely (in mg kg^{-1}), La (36.6), Ce (73), Pr (8.55), Nd (31.3) and Sm (6.83). W2 shows the highest concentrations of HREE, namely (in mg kg^{-1}), Eu (1.86), Gd (7.15), Tb (1.29), Dy (6.92), Ho (1.37), Er (3.61), Tm (0.57), Yb (3.36) and Lu (0.5). However, similar concentrations were also detected in W1.

4. Discussion

4.1. Concentration of critical elements in iron metallurgy slag

Slag composition is dependent on ore composition and metallurgical process. The main chemical components of slags, and their minimum and maximum values, are listed in Table 3. They differ for steelmaking- and blast-furnace slags due to the different composition and origin of the input materials. However, to maintain their physical properties, the contents shown in Table 3 cannot be exceeded during the steelmaking- or blast furnace processes (Janke et al. 2006; Juenger et al. 2006).

The concentrations of critical elements such as Nb, Ta and REE are usually not monitored in metallurgical slags. Comparison of the compositions of slags produced by different metallurgical processes and over a wide time span (historical to present) gives an overview of the concentrations of these elements. The concentrations of REE in blast-furnace slags are several times higher than in those described by, e.g. Gutiérrez- Gutiérrez

TABLE 2

Participation of the critical elements Nb, Ta and REE in the chemical composition of slags

Element /mg kg ⁻¹	Steelmaking slag					Blast furnace slag					Electric- arc furnace slag				Ladle furnace slag		
	S1	S2	JL1	JL2	JM1	JM2	B1	B2	W1	W2	W3	W4	W5	JL3	JL4	EAF	LF
Nb	30.4	24.1	n.a	n.a	21.9	5.4	0.6	1.5	5.5	8.3	15	11	5.2	n.a	n.a	146	2.5
Ta	1	1	12.4	6.8	0.8	0.1	0.1	0.3	0.5	0.8	1.1	0.8	0.6	2.6	b.d	2.2	0.2
Sc	1	b.d	1.7	2	5	7	9	11	14	15	14	13	14	17	15.4	1	3
Y	3.9	4.2	4	7	16.8	18.8	34.8	36.6	35.2	35.6	34.2	32.2	34	30	28	4.1	13.8
La	2.8	3.8	3.8	5.3	27.0	19.5	24.5	25.9	31.2	30.8	36.6	29.7	31.9	29.1	20.6	9.4	12.7
Ce	4.4	3.8	b.d	10	47.0	38.9	50.3	58.2	65.2	65.6	73	61.8	64.8	55	39	18.1	26.3
Pr	0.61	0.54	n.a	n.a	4.2	4.9	5.98	6.71	7.54	7.51	8.55	6.91	7.31	n.a	n.a	2	3.4
Nd	2.3	2	b.d	b.d	14.4	16.6	23.1	27.1	28.5	28.4	31.3	25.7	27.6	19	b.d	8.4	12.4
Sm	0.4	0.32	0.4	0.6	2.7	3.1	4.7	5.35	6.54	6.51	6.83	5.87	6.28	3.2	2.4	0.9	1.8
Eu	0.07	0.08	bd	0.2	0.74	0.62	1.44	1.57	1.8	1.86	1.7	1.74	1.76	1.1	0.8	0.15	0.31
Gd	0.42	0.41	n.a	n.a	2.6	2.8	4.75	5.35	7.09	7.15	6.96	6.34	7	n.a	n.a	0.8	1.6

Tb	0.06	0.07	b.d	b.d	0.4	0.4	0.82	0.9	1.3	1.29	1.17	1.13	1.25	b.d	b.d	0.1	0.2
Dy	0.4	0.31	n.a	n.a	2.2	2.3	4.86	5.26	6.92	6.92	6.28	6.1	6.58	n.a	n.a	0.9	1.6
Ho	0.08	0.09	n.a	n.a	0.4	0.5	0.91	1.03	1.32	1.37	1.23	1.19	1.29	n.a	n.a	0.1	0.3
Er	0.27	0.24	n.a	n.a	1.1	1.3	2.98	3.2	3.62	3.61	3.47	3.31	3.62	n.a	n.a	0.5	0.8
Tm	0.03	0.03	n.a	n.a	0.2	0.2	0.45	0.5	0.56	0.57	0.56	0.51	0.5	n.a	n.a	b.d	0.1
Yb	0.26	0.21	b.d	0.5	0.8	1.3	2.76	3.09	3.4	3.36	3.27	3	3.16	1.5	1.7	0.3	0.7
Lu	0.04	0.04	0.06	0.07	0.1	0.2	0.41	0.46	0.51	0.51	0.5	0.46	0.48	0.32	0.27	b.d	0.1
Σ REE (La-Lu)	12.14	11.94	4.26	16.67	103.84	92.62	127.96	144.62	165.5	165.46	181.42	153.76	163.53	109.22	54.77	41.56	62.31

S1, S2 – own measurements, steelmaking slag; JL1, JL2 – steelmaking slag (Jonczy, Lata 2013); B1, B2 – own measurements, blast furnace slag; W1, W2, W3, W4, W5 – blast furnace slag (Małoszowski 2009); JM1, JM2 – steelmaking slag (Jonczy 2014); JL3, JL4 – blast furnace slag (Jonczy, Lata 2013); EAF – electric-arc furnace slag (Jonczy 2014); LF – ladle-furnace slag (Jonczy 2014); n.a – not analyzed, b.d – below detection limit, bold – the highest measured concentrations

TABLE 3

Minimum- and maximum concentrations of main components in steelmaking slags (Geiseler 1996; Janke et al. 2006) and blast-furnace slags (Juenger et al. 2006)

Component	Steelmaking slag		Blast-furnace slag	
	minimum content (%)	maximum content (%)	minimum content (%)	maximum content (%)
SiO ₂	12	18	27	42
CaO	48	54	30	50
CaO ¹	1	10	n.a	n.a
Fe _{tot}	14	19	n.a	n.a
Al ₂ O ₃	n.a	n.a	5	33
MgO	1	4	0	21

¹ CaO – free lime

et al. (2015) in material from landfills. Contents of numerous elements (e.g. Sc) is higher than those noted in municipal solid-waste incineration residues, e.g. in bottom ash (Allegrini et al. 2014).

The question is whether the reported concentrations are high enough to make recovery economically viable. The grade of metal for exploitation is dependent on the ore value, market conditions and politics that determine the cut-off grade that makes production profitable (Evans 1993; Kelmendi, Azemi 2011). For example, the average grade for the Fen Rare Earth Element Deposit in Ulefoss, Norway, is 1.08%, whereas the cut-off grade is 0.8% for total REE (Lie, Østergaard 2014). Cut-off grades will vary from deposit to deposit. It is not only the richness of metal in ore and market prices that makes exploitation profitable, but also effective mining and processing techniques, valuable by-products and infrastructural costs. The concentration levels of the studied critical elements in the iron metallurgy slags do not reach values typical of low-grade ore concentrations. However, the slags contain less radioactive components (U, Th) than phosphogypsum (Kulczycka et al. 2016); this could facilitate their processing.

Though storing on heaps is one of the most common methods for waste disposal at minimum cost worldwide, it does bring problems such as leaching of hazardous materials into the environment. On the other hand, waste landfilling can be considered a source of potentially valuable resources such as e.g. constructions materials (Motz, Geiseler 2001) or metals (Hogland et al. 2004). Thus, landfills are increasingly seen as ‘local mines’ where valuable products were accumulated over time and thus excluded from further processing. When metal-containing waste is landfilled on a heap, metal mobility is limited (Jain et al. 2005). In case of metallurgical slags, a pH is ca 11 restricts the mobility and leaching of elements (Bozkurt et al. 1999).

Cossu et al. (1996) defined landfill mining as the extraction and processing of waste from active- and inactive landfills to protect the storage area, reduce its surface, eliminate a potential source of contamination, recover energy, recycle recovered materials, reduce

waste-management costs and redevelop the site. Van der Zee et al. (2004) define landfill mining as exploitation of landfill to recover metals and other raw materials.

4.2. Form of occurrence of critical elements in slag

The recovery of useful metals from landfilled waste is dependent on the physical- and chemical properties of the waste materials (Quaghebeur et al. (2010). It is influenced by the age of the waste and its susceptibility to phase transformation and degradation over time.

In the slags described above, the highest concentrations of REE occur in the blast-furnace slags characterized by the longest period of disposal (W1, W2, W3). However, it is difficult to show evidence that disposal time influences the concentration of REE. Also, no correlation was noted between pore size or slag crystallinity and the concentration of critical elements. Mineral composition is of much greater significance in this regard.

As distinct minerals rich in critical elements were not identified in the slags, it is possible to consider view them as dispersed in different mineral phases. The main mineral phases in the blast-furnace slags B1 and B2 are åkermanite, gehlenite, wollastonite, rankinite and, in smaller quantities, perovskite, MnS, titanite and lime (Kasina et al. 2014). The blast-furnace slags described by Jonczy and Lata (2013) were mostly composed of melilite-group minerals (åkermanite and gehlenite), quartz, and wollastonite whereas, in those from Kuźnice, clinopyroxene and leucite were main mineral phases. These samples also contain significant contents of glassy material.

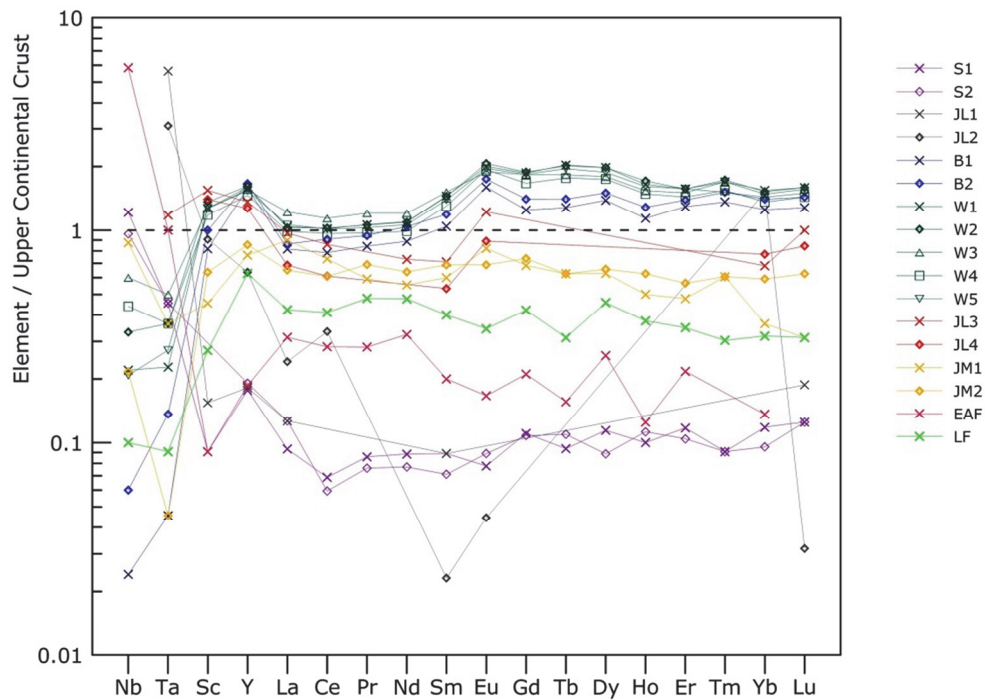


Fig. 1 UCC-normalized Nb, Ta and REE distribution pattern of Taylor and McLennan (1985).

The steelmaking slags S1 and S2 are composed mostly of larnite, srebrodolskite, wüstite with, in addition, lime, metallic iron, calcite and portlandite (Kasina et al. 2014). Similar components occur in the steelmaking slags JL1 and JL2 (Jonczy, Lata 2013). The diverse mineralogical compositions of the EAF and LF slags include many phases such as glass, metallic alloys, Ca and Mn sulfides, Fe, Mn, Mg, Ca oxides and their solid solutions, Ca ferrites, Ca silicates and aluminosilicates (melilite group minerals), Fe, Ca, Mg, Al hydroxides, Ca carbonates and Ca sulfates (see Jonczy 2014).

Nb, Ta and REE co-exist but also substitute for Ca which is abundant in both steelmaking and blast-furnace slags. They can also substitute for Fe which is abundant in the steelmaking slags. Since the concept of 'cut-off grade' involves many factors, and does not apply to existing deposits of the critical elements under consideration, it seems an unlikely useful parameter by which to define slag potential for valuable metal recovery. Thus, to evaluate the chemical-composition variability and to assess the potential contents of Nb, Ta and REE in the slags, the data were normalized relative to the average upper-crust composition (UCC; Taylor, McLennan 1985), to the North American Shale Composite (NASC; Gromet et al. 1984) and to average chondrite (Schmidt et al. 1963).

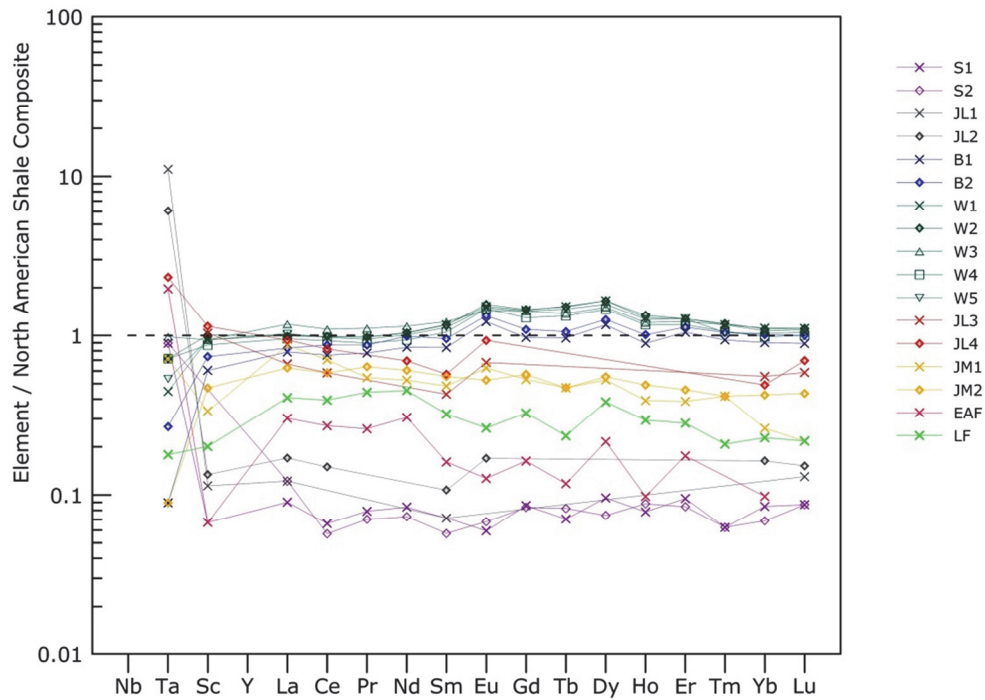


Fig. 2 NASC-normalized Nb, Ta and REE distribution pattern of Gromet et al. (1984).

Only a slight enrichment of Nb and Ta was noted in the steelmaking slags compared to the UCC whereas, in the blast-furnace slags, Y, Sc and HREE were enriched more clearly (Fig. 1). For the NASC normalization (Fig. 2), a significant enrichment for Ta in the steelmaking slags (JL1 and JL2) is evident as is a slight enrichment in HREE in blast-

furnace slags. In addition, practically all REE are enriched relative to average chondrite composition in all samples of both slag types (Fig. 3). The average abundances and, especially in the case of REE, their relative enrichment in relation to UCC, NASC and average chondrite composition in the slags may hint at their potential as a source of these elements.

The high volumes of dumped material, the limited metal mobility within dumps and their vertical stability in composition (Quaghebeur et al 2010; Gutiérrez- Gutiérrez et al 2015) are further factors that add to the potential for metal recovery from metallurgical dumps. However, to make the landfill mining profitable, costs and future benefits must be considered. Viability may well rely on effective recovery of critical metals in conjunction with other industrial raw materials.

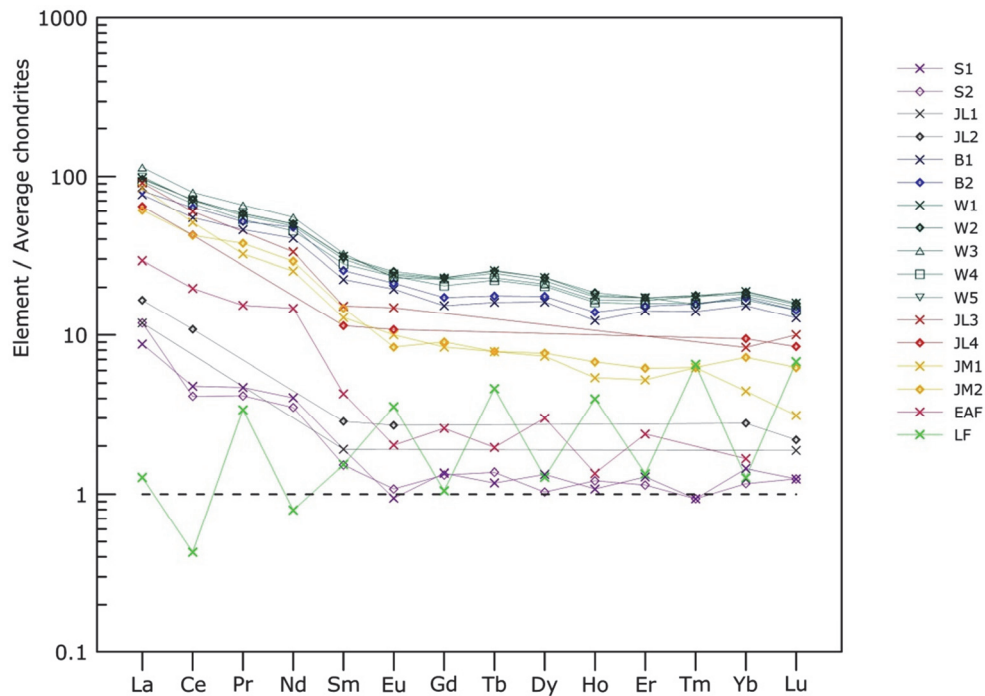


Fig. 3 Average chondrite-normalized Nb, Ta and REE distribution pattern of Schmidt et al. (1963).

4. Conclusion

1. Steelmaking and blast-furnace slags contain Nb, Ta and REE. The highest concentrations of Nb and Ta occur in steelmaking slags, whereas blast-furnace slags are richer in REE. In blast-furnace slags, HREE enrichment is especially high relative to UCC, NASC and average chondrite compositions.
2. There was no correlation between mineral composition, slag crystallinity and structure, and the concentration of critical elements.

3. The highest concentrations occur in slags with longer residence time on the heap. This may reflect the fact that, over time, restrictions concerning the composition of the input material in metallurgical processes and technological requirements have become stricter and, thus, slags characterized by longer disposal times contain the highest REE concentrations.
4. Because the mobility of elements in slags is limited due to high pH, their concentrations remain stable within the dump volume, facilitating recovery of useful elements and utilization of the disposal area.
5. The minimum cut-off grade is of less importance in the case of element recovery from slags. However, costs and benefits of metal recovery must be well estimated. Viable recovery is likely to require other materials as co-products or raw materials for the metallurgical- or building industry.
6. The concentrations of critical elements in the slags seem inadequate for profitable recovery.
7. The use of slags in, e.g. construction means that the potential recovery of critical elements is lost. Any potentially valuable concentrations of critical elements should be checked in advance of such usage.

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